Table 3-continued

9 days	39 (75.5)	39 (75.0)	39 (75.0)	38 (73.1)	38 (74.5)	42 (82.4)	39 (75.0)	38 (74.5)	42 (79.2)	39 (75.0)
Sample	A-21	A-22	A-23	A-24	A-25					
Water Absorption										
at 100% relative humidity										
1 day	0.3	0.1	0.1	0.3	0.2					
3 days	0.6	0.4	0.4	0.7	0.5					
5 days	0.8	0.7	0.6	1.0	0.8					
9 days	0.9	0.8	0.7	1.1	0.9					
Bending Strength (Kg/cm^2)*										
before absorption of water	51	52	52	52	51					
dipped in water										
0.5 minute	34 (66.7)	47 (90.4)	47 (90.4)	37 (71.2)	34 (66.7)					
60 minutes	32 (62.7)	37 (71.2)	37 (71.2)	34 (65.4)	32 (62.7)					
at 100% relative humidity										
3 days	39 (76.5)	41 (78.8)	41 (78.8)	40 (76.9)	39 (76.5)					
9 days	38 (74.5)	39 (75.0)	39 (75.0)	38 (73.1)	38 (74.5)					

*each parenthesized value indicates the strength retention ratio.

From the results shown in Table 3, it will readily be understood that when calcium silicate or calcium aluminosilicate is used as the calcium type filler reactant and the shaped structure of gypsum is treated with a polybasic acid such as oxalic acid, a very high water resistance is effectively imparted to the hardened shaped structure of gypsum.

EXAMPLE 3

This Example illustrates production of a hardened shaped structure having a high water resistance and an improved bending strength.

In the same manner as described in Example 1, 20 g of calcium oxide was added to 80 g of α-type gypsum hemihydrated and 75 ml of water was further added to the mixture to form a slurry. Then, 4 g of commercially available acrylamide of the reagent grade, 0.22 g of ammonium persulfate [$(NH_4)_2S_2O_8$] and 0.2 g of sodium sulfite ($Na_2SO_3.7H_2O$) were added to the slurry and the mixture was intimately blended to form a homogeneous paste. From this slurry, a hardened shaped structure of gypsum was prepared and treated with oxalic acid in the same manner as described in Example 1. Then, physical properties of the product were tested in the same manner as described in Example 1 to obtain the following results:

Filled Ca amount (C_1): 33.0%
Insoluble Ca amount (C_2): 2.6%
Pore volume (75–75000 Å): 0.490 ml/g
Pore volume (4000–10000 Å): 0.128 ml/g
Ratio of volume reduction in running water: 0%
Water absorption in the state dipped in water: 60 minutes: 20%
Water absorption at 100% relative humidity: 9 days: 0.7%
Bending strength:
- before absorption of water: 154 Kg/cm^2
- after 60 minutes' dipping in water: 127 Kg/cm^2
- strength retention ratio: 83%
- after 9 days' standing at 100% relative humidity: 130 Kg/cm^2
- strength retention ratio: 85%

From the foregoing results, it will readily be understood that when acrylamide is incorporated into a water-hardening composition comprising gypsum hemihyrate and a filler reactant such as calcium hydroxide, acrylamide is polymerized simultaneously with hardening of the gypsum composition and the hardened structure is treated with a polybasic acid such as oxalic acid, the bending strength (154 Kg/cm^2) of the resulting hardened shaped structure is much improved over the bending strength (53 Kg/cm^2) of the hardened shaped structure formed without incorporation of acrylamide (sample 1 in Example 1), while retaining the water resistance at a similar high level.

What we claim is:

1. A water-resistant shaped structure of gypsum comprising (A) calcium sulfate dihydrate formed by hardening of calcium sulfate capable of hydration reaction, (B) a calcium type filler for filling up spaces among crystalline particles of said calcium sulfate dihydrate and (C) a water-insoluble or hardly water-soluble calcium salt of a polybasic acid having a second stage dissociation constant of 10^{-3} to 10^{-10}, as measured at 25° C., said calcium type filler (B) being at least one calcium compound selected from the group consisting of calcium hydroxide, calcium carbonate, calcium silicate, calcium aluminosilicate, and non-water hardenable anhydrous gypsum and partially hydrated products thereof, wherein the amount of the calcium type filler (B) and the water-insoluble or hardly water-soluble calcium salt (C) is 15 to 75% based on the total amount of the components (A), (B) and (C) as calculated as calcium, the amount of the water-insoluble or hardly water-soluble calcium salt (C) is 1 to 30% based on the total amount of the components (A), (B) and (C) as calculated as calcium, the water-insoluble or hardly water-soluble calcium salt (C) is distributed predominantly in the surface portion of the shaped structure and is formed in situ in said shaped structure by reaction of said calcium type filler (B) with said polybasic acid or a water-soluble salt thereof, and said surface portion has a pore volume smaller than 0.50 ml/g in pores having a radius in the range of 75 to 75000 Å and a pore volume smaller than 0.20 ml/g in pores having a radius in the range of 4000 to 10000 Å.

2. A shaped structure as set forth in claim 1 wherein in the surface portion of the shaped structure of gypsum, the mode radius of pores is not larger than 0.5μ.

3. A shaped structure as set forth in claim 1 wherein the polybasic acid is oxalic acid, phosphoric acid or hexafluorosilicic acid.

4. A shaped structure as set forth in claim 1 wherein the shaped structure of gypsum further comprise a poly-